

Chemistry—a Topological Subject

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1 Introduction

Metric geometry is governed by the concepts of congruence of line segments and angles. In contrast, topology is the geometry of properties which remain invariant under topological mappings, *i.e.* mappings such that they and their inverses are single-valued and continuous. These maps may be expressed by groups of continuous functions. Topology is therefore a major division of abstract mathematics with applications in concrete situations that range from knots and knitting to systems of connected points such as railway networks, trees, and chemical formulae and to the properties of strange and complex surfaces such as the Moebius strip.¹

Various aspects of topology have been applied to structural and other problems in chemistry, but the aspect which has so far proved to be most useful is the theory of mathematical graphs.² Graphs are collections of points and lines, drawn so that pairs of the points are connected together. Such a graph may, for example, illustrate the operations of any symmetry group. It may also be a concise statement of our preconceptions about the connections (which may be independent of symmetry) within a system based, hopefully, on reasonable premises. To emphasize this dependence of the connectivity graph on our prejudices we reproduce in Figure 1 a religious graph which symbolically represents the Christian Trinity. This diagram expresses relationships in close accord with those embodied in a valence-bond description of ammonia—in both cases there is a concise statement of unprovable but established understanding of the main features of the system of interest. The special value of chemical graphs, however, is they may often also be used to obtain additional information about the system. Indeed, very powerful semi-empirical conclusions may frequently be obtained by the sympathetic use of the symmetry and topology of the problem,^{3,4} particularly in the cases of polygonal and polyhedral molecules and other chemical systems.⁵⁻⁹

¹ B. Mendelson, 'Introduction to Topology', Allyn & Bacon, Glasgow, 1968.

² D. H. Rouvray, *R.I.C. Rev.*, 1971, 4, 173.

³ H. H. Schmidtke, *Co-ordination Chem. Rev.*, 1967, 2, 3.

⁴ H. H. Schmidtke, *Internat. J. Quantum Chem., Symp.*, 1968, 2S, 101.

⁵ R. B. King, *J. Amer. Chem. Soc.*, 1970, 92, 7211, 7217.

⁶ H. H. Schmidtke, *Theor. Chim. Acta*, 1968, 9, 199.

⁷ A. Graovac, I. Gutman, N. Trinajstić, and T. Žirković, *Theor. Chim. Acta*, 1972, 26, 67.

⁸ S. F. A. Kettle and V. Tomlinson, *Theor. Chim. Acta*, 1969, 14, 175.

⁹ S. F. A. Kettle, *Theor. Chim. Acta*, 1966, 4, 150.

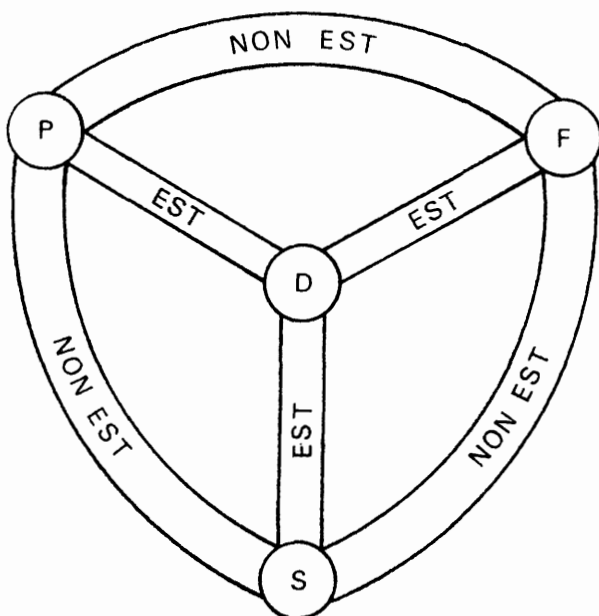


Figure 1 *The Shield of the Christian Trinity*

We shall now show, mainly by reference to square-planar and tetrahedral molecules, how the general solution of some topological problems may be applied to a variety of situations of chemical interest (Section 2). In Section 3 we give detailed examples designed to help the reader to apply similar methods to other systems of interest. The information which we shall obtain consists of energy levels that refer to equivalent components of the system. These are calculated algebraically in terms of a limited number of connectivity parameters variously called 'resonance integrals', 'interaction constants', 'coupling constants', *etc.* according to the context. In the simplest cases only a single connectivity parameter, K , may be needed, and the calculated energy levels take the form $E_i = E_0 + c_i K$. Much may be deduced even from knowledge of the sign and order of magnitude of K . Secondly, in a case with a manifold of energy levels, the empirical determination of a single energy level separation suffices to determine the energies of all levels in the manifold. In general, useful information can always be obtained so long as the number of important and distinctive parameters does not exceed the number of relevant experimental data.

2 Connectivity in Familiar Chemical Ideas

The manner in which a molecule is thought to be connected together enables us to select those interactions which are important and those which are of little significance. Thus both CH_4 and P_4 have the symmetry of a regular tetrahedron,

but the topology of the bonding schemes which are intuitively required by the chemist are quite different. The topology of the valence bonds in phosphorus is, however, the same as that of the bonding-pair electron repulsions and the proton nuclear spin coupling in methane.

In Figure 2 we show the structure of these and other tetrahedral molecules

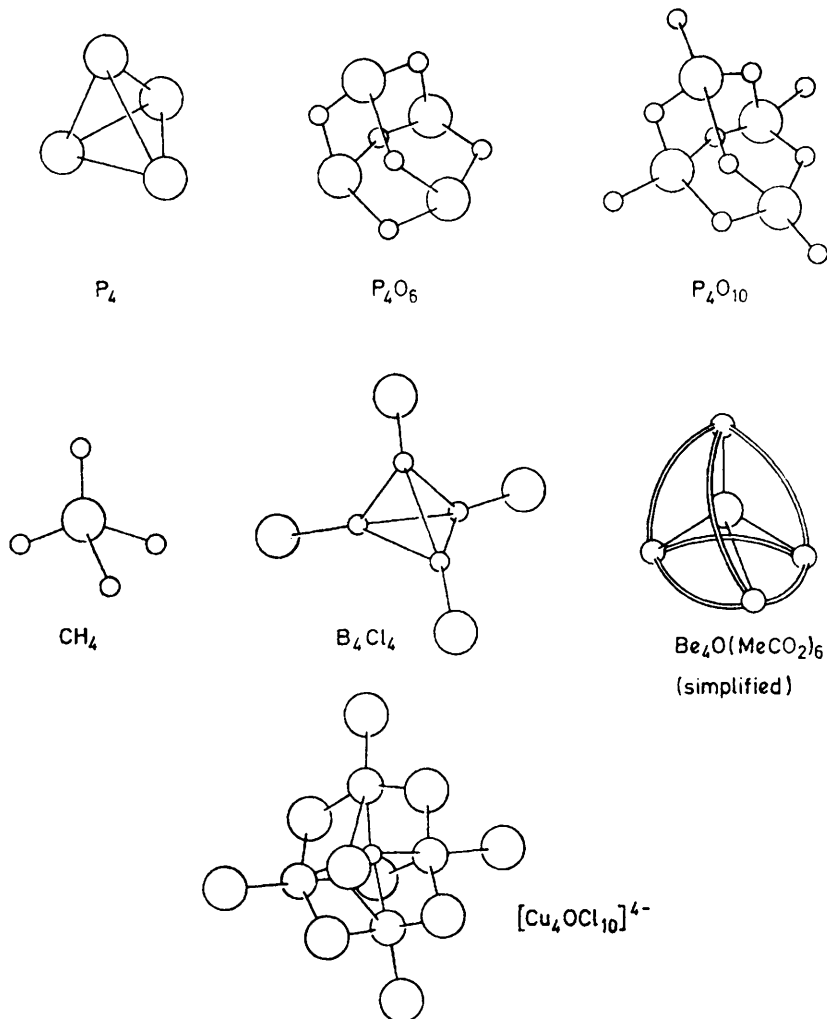


Figure 2 Topological diagrams for tetrahedral molecules

and ions with a diversity of bond connectivity graphs. The high, T_d , symmetry of each compound enables us to solve problems within each set of equivalent

atoms exactly in terms of the interaction between any pair of equivalent atoms. Nevertheless, we can see immediately that, in some cases such as the $[\text{Cu}_4\text{OCl}_{10}]^{4-}$ ion, the interactions between equivalent atoms are unlikely to be the most important! Rather we would expect that the important interactions affecting the properties of the $[\text{Cu}_4\text{OCl}_{10}]^{4-}$ ion are those between the set of four copper atoms and each of the other sets of atoms. Clearly topology will not help us much in this case, whereas it is likely to dominate the discussion of all of the properties of P_4 . There are many other cases in which topologically distinct figures have a common symmetry.⁵ A familiar example is provided by the pairs of Platonic solids of O_h and I_h symmetry.

A decision on the topology of a chemical problem may be of more fundamental importance than a decision on its real or approximate symmetry, since these decisions must be based on a realistic appraisal of energetic factors. Consider the bonding in 'octahedral' transition-metal complexes. True octahedral complexes are not common but, nevertheless, the most important properties of the majority of distorted complexes may be interpreted in terms of O_h symmetry, to which modifications due to small distortions are added if required. The recognition of a superclass of 'octahedral' complexes is itself essentially a topological perception. In these metal complexes the body of evidence leads us to argue that the magnitude of the metal–ligand σ -bonding is such as to give rise to interesting and measurable effects with decreasingly important roles assigned to π -bonding, distortions, and ligand–ligand bonding interactions.^{10,11}

The relative order of magnitude of these interactions is similar in unsaturated organic molecules, but in these cases the bonding is generally much stronger and we rarely encounter a partially filled σ -orbital. Rather it is the π -orbital set which gives rise to the bulk of the properties of interest and it is the topology of the π -bonding which forms the basis of Hückel theory in two or three dimensions.⁸

Although many chemical bonds are of similar strengths, their stretching frequencies often differ widely because of kinetic-energy effects. This leads to the recognition of characteristic group frequencies in infrared spectroscopy. For similar bonds in a variety of molecules, modifications to the characteristic frequency may be meaningfully interpreted in terms of the relative strengths of the bonds. Conversely, the restoring forces for most bending and deformation modes are dominated by electron-repulsion effects of a different topology. Thus the in-plane C–H deformation frequencies of aromatic compounds are much higher than those associated with the out-of-plane modes. Molecular vibrations may be of the same intrinsic energy either accidentally or as a necessary consequence of symmetry. These vibrations will then couple together relatively strongly if the topological relationship between the groups is sufficiently important for them to 'know' one another, and the coupling may be recognized by the appearance of a manifold of frequencies centred on the group frequency;¹² indeed, the average-

¹⁰ H. B. Gray, *J. Chem. Educ.*, 1964, 41, 2.

¹¹ S. F. A. Kettle, *J. Chem. Educ.*, 1966, 43, 652.

¹² G. Herzberg, 'Molecular Spectra and Molecular Structure: Volume II, Infra-red and Raman Spectra of Polyatomic Molecules', Van Nostrand, New York, 1945.

frequency rule is a valuable aid to vibrational assignments.¹³ Furthermore, there are certain groupings of symmetry-related vibrations which have a characteristic topology determined by their number and geometrical relationship. Thus, for example, even the vibrations of a methyl group may often be readily distinguished from related vibrations of a methylene group.¹⁴

An intrinsically topological topic is the interpretation of the 'coupling' between nuclear-spin moments, which is an essential feature of the analysis of high-resolution n.m.r. spectra.¹⁵ Each significant coupling constant defines a connection which is a component part of the overall topology of the problem. This connection has a peculiar form, because it has $(2S_i + 1)(2S_j + 1)$ sub-components which lead to the familiar dipolar coupling term, $-J_{ij} S_i S_j$, in the effective Hamiltonian used to interpret the system.* Analogous descriptions apply to the hyperfine interactions in e.s.r. spectroscopy and to the bonding process itself, which may also be thought of in terms of a dipolar electron-spin coupling.

Unfortunately, these spin-coupling problems are difficult to illustrate concisely because of the large number of spin functions required to describe systems of interest, and since we have previously given the energy levels arising from spin-spin coupling for a large range of molecular symmetries and topological situations,¹⁶ we shall omit examples of this type from Section 3 below. It should also be noted that there are many similarities within all systems in which the coupling of angular momenta is involved. For example, an effective connectivity scheme underlies the formulation of Russell-Saunders coupling, spin-orbit coupling, *jj*-coupling, *etc.*

Finally, we comment on the fact that, after the recognition of elements and atoms, the most powerful perception in chemistry has been the recognition of the chemical bond. Clearly then, at least implicitly, chemists like to think of chemistry as a topological subject.

3 General Solution of Some Simple Topological Problems

In this section we shall be concerned with the solution of some simple problems associated with tetrahedral and square-planar molecules and in illustrating the more general applicability of these solutions with a few other examples. We arbitrarily choose to discuss vibrations of tetrahedral molecules and the Hückel energies of the square system in the most detail.

*An interesting feature of the coupling constants in n.m.r. spectroscopy concerns the nature of the coupling between equivalent nuclei. This can be neglected because the selection rules appropriate to the normal n.m.r. experiment rigidly exclude transitions between energy levels which differ in this coupling energy. The complexity of the problem is thereby often strikingly reduced by neglect of these connections although, in many cases, the neglected interactions are amongst the strongest for that molecule.

¹³ W. J. Lehmann, *J. Mol. Spectroscopy*, 1964, 7, 1.

¹⁴ A. D. Cross, 'An Introduction to Practical Infra-red Spectroscopy', 2nd Edn., Butterworths, London, 1964.

¹⁵ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon, Oxford, 1965.

¹⁶ R. W. Jotham and S. F. A. Kettle, *Inorg. Chim. Acta*, 1970, 4, 145.

A. Tetrahedral Systems.—The T_d character table (Table 1) will be required for the problems discussed in detail below.

Table 1 T_d Character table

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Rotations	Vectors	Vector products
A_1	1	1	1	1	1			$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1			xyz
E	2	0	2	0	0			$(2z^2 - x^2 - y^2)$ $x^2 - y^2$
T_1	3	-1	-1	-1	1	(R_x, R_y, R_z)		
T_2	3	-1	-1	1	-1		(x, y, z)	(xy, xz, yz)

(i) **C—H Stretching Vibrations of CH_4 .** The C—H stretching vibrations of methane are readily shown to transform as $A_1 + T_2$. The non-degenerate mode is active only in the Raman spectrum whereas the triply degenerate mode may be observed in both the i.r. and the Raman spectra. The observed modes of T_2 symmetry are not quite pure stretching vibrations because deformation modes of the same symmetry are mixed in slightly and the vibrations must be orthogonal to the T_2 translations, but to a very good approximation the modes described as the A_1 and T_2 C—H stretching vibrations are observed at 2914 and 3020 cm^{-1} , respectively.¹² If we write the four individual C—H stretching motions as r_1 — r_4 we may readily show that the appropriate orthonormal combinations of these unit vectors are given by (1).

$$\begin{array}{l}
 A_1 \\
 T_2
 \end{array}
 \left\{
 \begin{array}{l}
 \psi_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4) \\
 \psi_2 = \frac{1}{2}(r_1 + r_2 - r_3 - r_4) \\
 \psi_3 = \frac{1}{2}(r_1 - r_2 + r_3 - r_4) \\
 \psi_4 = \frac{1}{2}(r_1 - r_2 - r_3 + r_4)
 \end{array}
 \right.
 \quad (1)$$

If a negative coefficient indicates a compression, we can readily see that these expressions are not exact, for each of the T_2 modes should include a slight opposing motion of the carbon atom to maintain the centre of gravity, and we emphasize that the observed frequencies are those of the *normal* modes rather than the symmetry modes. Nevertheless, the functions ψ_1 — ψ_4 may be used to extract useful information from the observed frequencies. To do this we must consider the energy appropriate to a *single* C—H stretching motion in CH_4 which we shall call ν and the interaction energy between each pair of stretching motions which we shall call ν' . In tetrahedral CH_4 all the interactions are of the same type. We may represent this set of interactions by the topological matrix (2).

$$\begin{array}{ccccc}
 & r_1 & r_2 & r_3 & r_4 \\
 r_1 & 0 & 1 & 1 & 1 \\
 r_2 & 1 & 0 & 1 & 1 \\
 r_3 & 1 & 1 & 0 & 1 \\
 r_4 & 1 & 1 & 1 & 0
 \end{array}
 \quad (2)$$

It follows, then, that the eigenvalues (*i.e.* the observed frequencies) of this problem may be obtained by solving the secular equation (3).

$$\begin{vmatrix} \nu - E & \nu' & \nu' & \nu' \\ \nu' & \nu - E & \nu' & \nu' \\ \nu' & \nu' & \nu - E & \nu' \\ \nu' & \nu' & \nu' & \nu - E \end{vmatrix} = 0 \quad (3)$$

This equation is grossly simplified if we utilize the symmetry functions $\psi_1-\psi_4$. We first write out a new energy matrix (4) for the $\langle r_i \| r_j \rangle$ in terms of

$$\begin{array}{cccc} & \langle r_1 | & \langle r_2 | & \langle r_3 | & \langle r_4 | \\ \begin{array}{l} | r_1 \rangle \\ | r_2 \rangle \\ | r_3 \rangle \\ | r_4 \rangle \end{array} & \begin{array}{l} \nu \\ \nu' \\ \nu' \\ \nu' \end{array} & \begin{array}{l} \nu' \\ \nu \\ \nu' \\ \nu' \end{array} & \begin{array}{l} \nu' \\ \nu' \\ \nu \\ \nu' \end{array} & \begin{array}{l} \nu' \\ \nu' \\ \nu' \\ \nu \end{array} \end{array} \quad (4)$$

ν and ν' . We now transform the matrix (4) into the matrix (6) by either a simple direct expansion technique or, more rapidly, by proceeding through the intermediate matrix (5). Thus, for example:

$$\begin{aligned} \langle \psi_1 \| \psi_3 \rangle &= \langle \frac{1}{2}(r_1 + r_2 + r_3 + r_4) \| \frac{1}{2}(r_1 - r_2 + r_3 - r_4) \rangle \\ &= \frac{1}{4} [\langle r_1 \| r_1 \rangle - \langle r_2 \| r_2 \rangle + \langle r_3 \| r_3 \rangle - \langle r_4 \| r_4 \rangle \\ &\quad - \langle r_1 \| r_2 \rangle + \langle r_1 \| r_3 \rangle - \langle r_1 \| r_4 \rangle \\ &\quad + \langle r_2 \| r_1 \rangle + \langle r_2 \| r_3 \rangle - \langle r_2 \| r_4 \rangle \\ &\quad + \langle r_3 \| r_1 \rangle - \langle r_3 \| r_2 \rangle - \langle r_3 \| r_4 \rangle \\ &\quad + \langle r_4 \| r_1 \rangle - \langle r_4 \| r_2 \rangle + \langle r_4 \| r_3 \rangle] \\ &= 0 \text{ [after substituting for each } \langle r_i \| r_j \rangle \text{ the appropriate element of} \\ &\quad \text{matrix (4)}] \end{aligned}$$

$$\begin{aligned} \langle \psi_2 \| r_2 \rangle &= \frac{1}{2} \langle (r_1 + r_2 - r_3 - r_4) \| r_2 \rangle \\ &= \frac{1}{2} [\langle r_1 \| r_2 \rangle + \langle r_2 \| r_2 \rangle - \langle r_3 \| r_2 \rangle - \langle r_4 \| r_2 \rangle] \\ &= \frac{1}{2} (\nu - \nu') \end{aligned}$$

$$\begin{array}{cccc} & \langle r_1 | & \langle r_2 | & \langle r_3 | & \langle r_4 | \\ \begin{array}{l} | \psi_1 \rangle \\ | \psi_2 \rangle \\ | \psi_3 \rangle \\ | \psi_4 \rangle \end{array} & \begin{array}{l} \frac{1}{2}(\nu + 3\nu') \\ \frac{1}{2}(\nu - \nu') \\ \frac{1}{2}(\nu - \nu') \\ \frac{1}{2}(\nu - \nu') \end{array} & \begin{array}{l} \frac{1}{2}(\nu + 3\nu') \\ \frac{1}{2}(\nu - \nu') \\ \frac{1}{2}(\nu' - \nu) \\ \frac{1}{2}(\nu' - \nu) \end{array} & \begin{array}{l} \frac{1}{2}(\nu + 3\nu') \\ \frac{1}{2}(\nu' - \nu) \\ \frac{1}{2}(\nu - \nu') \\ \frac{1}{2}(\nu' - \nu) \end{array} & \begin{array}{l} \frac{1}{2}(\nu + 3\nu') \\ \frac{1}{2}(\nu' - \nu) \\ \frac{1}{2}(\nu' - \nu) \\ \frac{1}{2}(\nu - \nu') \end{array} \end{array} \quad (5)$$

$$\begin{array}{cccc} & \langle \psi_1 | & \langle \psi_2 | & \langle \psi_3 | & \langle \psi_4 | \\ \begin{array}{l} | \psi_1 \rangle \\ | \psi_2 \rangle \\ | \psi_3 \rangle \\ | \psi_4 \rangle \end{array} & \begin{array}{l} \nu + 3\nu' \\ 0 \\ 0 \\ 0 \end{array} & \begin{array}{l} 0 \\ \nu - \nu' \\ 0 \\ 0 \end{array} & \begin{array}{l} 0 \\ 0 \\ \nu - \nu' \\ 0 \end{array} & \begin{array}{l} 0 \\ 0 \\ 0 \\ \nu - \nu' \end{array} \end{array} \quad (6)$$

The solution of the corresponding secular equation (7) is trivial.

$$\begin{vmatrix} \nu + 3\nu' - E & 0 & 0 & 0 \\ 0 & \nu - \nu' - E & 0 & 0 \\ 0 & 0 & \nu - \nu' - E & 0 \\ 0 & 0 & 0 & \nu - \nu' - E \end{vmatrix} = 0 \quad (7)$$

Thus the eigenvalues $\nu + 3\nu'$ and $\nu - \nu'$ (thrice) correspond to the A_1 and T_2 modes, respectively. If these are equated to the observed frequencies, we find that, for CH_4 , $\nu = 2994 \text{ cm}^{-1}$ and $\nu' = -26 \text{ cm}^{-1}$. The quantity ν should be comparable for all types of C—H bond in similar molecules. We see also that the interaction between two stretching motions is not very great in this case (as in all hydrocarbons), reflecting the very high localization of the electrons in the well separated bonds. The sign of ν' is often of great interest; a negative sign indicates that the out-of-phase motion is of higher frequency than the in-phase motion (*i.e.* the stretching of one bond facilitates the stretching of the adjacent bond in the case of CH_4).

(ii) *The Vibrations of P_4 .* The number of vibrations of CH_4 is nine, whereas P_4 has only six vibrations which classify as $A_1 + E + T_2$. These are observed at 606 (Raman, polarized), 363 (Raman), and 465 cm^{-1} (Raman, i.r.), respectively. It is clear that we could treat the A_1 and T_2 modes as the radial motions of the phosphorus atoms with respect to the centre of gravity. This discussion would parallel that given in (i) and we calculate $\nu = 500 \text{ cm}^{-1}$ and $\nu' = 35 \text{ cm}^{-1}$. The interaction between two of these radial stretches now, however, represents a stretching of a P—P bond and it is not surprising that these radial stretches hinder one another. To complete a discussion on this basis the E mode would have to be described independently in terms of the tangential motions of the phosphorus atoms.

Alternatively, it is possible to set up this problem in terms of an *edge* basis, for the six P—P bonds transform as $A_1 + E + T_2$. The *same* vibrations may be described in terms of either these P—P stretches or the radial and tangential motions of the vertices both for CH_4 and for P_4 . Intuitively, however, we prefer an edge topology for P_4 and a radial one for CH_4 . The interaction matrix for the six P—P bond stretches S_{12} — S_{34} is given in (8).

$$\begin{array}{l} \langle S_{12} | \\ | S_{12} \rangle \\ \langle S_{13} | \\ | S_{13} \rangle \\ \langle S_{14} | \\ | S_{14} \rangle \\ \langle S_{23} | \\ | S_{23} \rangle \\ \langle S_{24} | \\ | S_{24} \rangle \\ \langle S_{34} | \\ | S_{34} \rangle \end{array} \begin{array}{cccccc} \langle S_{12} | & \langle S_{13} | & \langle S_{14} | & \langle S_{23} | & \langle S_{24} | & \langle S_{34} | \\ \nu & \nu_c & \nu_c & \nu_c & \nu_c & \nu_t \\ \nu_c & \nu & \nu_c & \nu_c & \nu_t & \nu_c \\ \nu_c & \nu_c & \nu & \nu_t & \nu_c & \nu_c \\ \nu_c & \nu_c & \nu_t & \nu & \nu_c & \nu_c \\ \nu_c & \nu_t & \nu_c & \nu_c & \nu & \nu_c \\ \nu_t & \nu_c & \nu_c & \nu_c & \nu_c & \nu \end{array} \quad (8)$$

From standard group-theoretical arguments we find that the symmetry modes are as shown in (9).

$$\begin{aligned}
 A_1 \quad \psi_1 &= \frac{1}{\sqrt{6}} (S_{12} + S_{13} + S_{14} + S_{23} + S_{24} + S_{34}) \\
 E \quad \left\{ \begin{aligned} \psi_2 &= \frac{1}{\sqrt{12}} (2S_{12} - S_{13} - S_{14} - S_{23} - S_{24} + 2S_{34}) \\ \psi_3 &= \frac{1}{2} (S_{13} - S_{14} - S_{23} + S_{24}) \end{aligned} \right. \\
 T_2 \quad \left\{ \begin{aligned} \psi_4 &= \frac{1}{\sqrt{2}} (S_{12} - S_{34}) \\ \psi_5 &= \frac{1}{\sqrt{2}} (S_{13} - S_{24}) \\ \psi_6 &= \frac{1}{\sqrt{2}} (S_{14} - S_{23}) \end{aligned} \right. \quad (9)
 \end{aligned}$$

If we use these functions to diagonalize the matrix (6) and equate the solutions to the observed frequencies we find

$$\begin{aligned}
 A_1 \quad \nu + 4\nu_c + \nu_t &= 606 \text{ cm}^{-1} \\
 E \quad \nu - 2\nu_c + \nu_t &= 363 \text{ cm}^{-1} \\
 T_2 \quad \nu - \nu_t &= 465 \text{ cm}^{-1}
 \end{aligned}$$

Solution of these equations gives $\nu = 454$, $\nu_c = 41$, and $\nu_t = -11 \text{ cm}^{-1}$. In this case, if the T_2 translation is neglected (and the T_2 functions ψ_4 — ψ_6 are readily seen to be virtually free of a translational element), a complete description is obtained in terms of three independent parameters ν , ν_c , and ν_t by the application of symmetry to the topological matrix. As there are three observable frequencies a complete semi-empirical description is obtained for this problem.

(iii) *Molecular Orbitals of CH₄*. If the 1s electrons of the carbon atom are neglected, the basis set of atomic orbitals for CH₄ consists of the 2s and 2p orbitals of the carbon atom, which transform as A_1 and T_2 respectively in T_d symmetry. The four 1s ligand group orbitals of the hydrogen atom also transform as $A_1 + T_2$.¹¹ This set of four orbitals bears the same symmetric and topological relationships as the four C—H stretching motions of CH₄. If we call the four 1s orbitals ϕ_1 — ϕ_4 , then the A_1 and T_2 ligand group orbitals are isomorphous to the set (1), and we may parallel the whole of the discussion in (i) by replacing each ν_{ij} by a H_{ij} . This calculation is, however, of little significance in this case because the off-diagonal H_{ij} are virtually zero unless the pairs of 1s orbitals overlap appreciably. As a result of the negligible values of the off-diagonal elements the A_1 and T_2 ligand group orbitals are essentially isoergic. Instead, the analysis of this problem is dominated by the interactions between the 2s and 2p orbitals of the carbon atom and the hydrogen orbitals. As the set of ligand group orbitals

isomorphous to (1) contain equal contributions from each atom, the A_1 and the three T_2 bonds will also involve these equal contributions so that the tetrahedral symmetry is maintained in the delocalized description. The valence-bond description, involving sp^3 hybrid orbitals on the carbon atoms, remains useful and popular precisely because it provides a simple concept which may be directly related to the intuitively perceived topological requirements of this problem and related ones.

(iv) *Molecular Orbitals of P_4* . Unlike the case of CH_4 , topological considerations play a great part in the discussion of the molecular orbital diagram of P_4 , because the overlap of the symmetry-related atomic orbitals in this molecule is not negligible. If we consider each phosphorus atom separately and select as a basis set of atomic orbitals the $3s$ and $3p$ orbitals only, we can consider each of these sets to be subject to a perturbing field of C_{3v} symmetry due to the other three phosphorus atoms. Defining local z -axes accordingly we see that each $3s$ and $3p_z$ orbital may be classified as A_1 and each pair of $3p_x$ and $3p_y$ orbitals as E in the C_{3v} symmetry. One sp_z hybrid lies inside the tetrahedron and the second lies outside. The latter hybrids accommodate the two essentially non-bonding electrons on each phosphorus atom. The other set of four sp_z hybrid orbitals and the $3p_x$ and $3p_y$ orbitals are responsible for 'central' and 'edge' bonding of the phosphorus atoms in the tetrahedron. The set $4 \times (\text{local } A_1)$ transforms as $A_1 + T_2$ in T_d symmetry, whereas the set $4 \times (\text{local } E)$ transforms as $E + T_1 + T_2$.

Within each of these sets the splitting may be decided entirely on topological grounds, and explicit use of functions derived by symmetry leads to a rapid solution of this part of the problem. The assessment of the interaction between the T_2 states can only be decided on energetic grounds. This general solution of topological matrices by symmetry arguments forms the basis of Hückel theory in two dimensions and is readily extended to three. We have already solved the central bonding portion twice! The solutions are contained in the matrix (6) if we replace ν and ν' by the Hückel parameters α_c and β_c (c indicating central and ψ_1 — ψ_4 are appropriate combinations of the sp_z hybrid orbitals isomorphic to the equations (1). α and β are regarded as intrinsically negative (*i.e.* binding) quantities so that the A_1 orbital at $\alpha_c + 3\beta_c$ is more stable than the three T_2 orbitals at $\alpha_c - \beta_c$. (The latter should not be regarded as antibonding, but as less stable than their parent orbitals.) In this case we may reasonably assume the topological basis to be mainly edge bonding, although the local p_x and p_y orbitals lie largely outside the tetrahedron. Although we may readily derive the representation of the set of eight tangential orbitals, it is difficult to relate the pairs of orbitals at each corner neatly to the three edges that meet there. We refer the interested reader to the discussion of this peripheral and π -bonding problem by Schmidtke for its detailed solution.⁶ He found that the complete orbital energy sequence for the twelve p orbitals is $A_1 < T_2 < E < T_1 < T_2$. Inclusion of the $3s$ orbitals stabilizes this A_1 orbital further but destabilizes the T_2 orbitals slightly.

The calculation shows very simply that, in addition to the non-bonding

electrons in external A_1 and T_2 orbitals, the remaining twelve valence electrons of P_4 are accommodated in bonding orbitals of A_1 , E , or T_2 symmetry. The A_1 bonding orbital has an entirely central character whereas the E orbitals are peripheral. The T_2 bonding orbitals have a mixed central and peripheral nature. The particular admixture is determined by the relative magnitudes of the 'resonance' integrals, β_i . Finally we may remark that the six 'valence bonds' of P_4 transform as the six edges of a tetrahedron, *i.e.* as $A_1 + E + T_2$. The reproduction of six bonding orbitals spanning just these representations reflects, ultimately, the intuitive choice of an edge topology for the important interactions.

Kettle has given a very similar discussion of P_4 in which 12 bonding electrons are found in edge orbitals of types $A_1 + E + T_2$ whereas the remaining eight electrons are found in face-bonding orbitals of type $A_1 + T_2$.⁹ These face orbitals correspond to a mixture of our central bonding orbitals and external non-bonding orbitals. It is important to realize that the topological basis of the problem can be ambiguous for many *three*-dimensional molecules.⁸

(v) *Stretching Vibrations of Deuteriomethanes.* A small distortion of a tetrahedral molecule which does not destroy one of the three-fold axes usually leads to C_{3v} symmetry. The topology of the system may well be invariant to this distortion, so that we must explore the consequences of introducing an energetic inequivalence into the same topological framework.

A particularly interesting example is provided by the vibrational spectrum of CH_3D . The reduced mass of a C—D bond pair is almost $\sqrt{2}$ times as large as that of a C—H bond pair [more accurately $\mu_D/\mu_H = \sqrt{(13/7)}$], and C—D stretching vibrations are observed near 2200 cm^{-1} whereas the corresponding C—H modes occur at about 3000 cm^{-1} . Nevertheless, the electronic forces in CH_3D cannot differ greatly from those in CH_4 ; in particular it seems very likely that the coupling between C—H stretching motions and C—D stretching motions will be very similar to that between two C—H stretching motions. We therefore replace the matrix (4) of the CH_4 problem by (10) in which we expect $\nu'_{H-H} \approx \nu'_{H-D}$ but $\nu_H \approx \sqrt{(13/7)}\nu_D$.

$$\begin{array}{cccc}
 & \langle r_1 | & \langle r_2 | & \langle r_3 | & \langle r_4 | \\
 | r_1 \rangle & \nu_H & \nu'_{H-H} & \nu'_{H-H} & \nu'_{H-D} \\
 | r_2 \rangle & \nu'_{H-H} & \nu_H & \nu'_{H-H} & \nu'_{H-D} \\
 | r_3 \rangle & \nu'_{H-H} & \nu'_{H-H} & \nu_H & \nu'_{H-D} \\
 | r_4 \rangle & \nu'_{H-D} & \nu'_{H-D} & \nu'_{H-D} & \nu_D
 \end{array} \quad (10)$$

Linear combinations of r_1 — r_4 of $2A_1 + E$ symmetry are readily constructed from the C_{3v} character table (Table 2) and are given by (11).

Table 2 C_{3v} Character table

C_{3v}	E	$2C_3$	$3\sigma_v$	Rotations	Vectors	Vector products
A_1	1	1	1		z	$2z^2 - x^2 - y^2,$ $x^2 + y^2 + z^2$
A_2	1	1	-1	R_z		
E	2	-1	0	(R_x, R_y)	(x, y)	$(xz, yz), (xy, x^2 - y^2)$

$$\begin{aligned}
 A_1 \psi_1 &= |r_4\rangle \\
 A_1 \psi_2 &= \frac{1}{\sqrt{3}}(|r_1\rangle + |r_2\rangle + |r_3\rangle) \\
 E \begin{cases} \psi_3 = \frac{1}{\sqrt{6}}(2|r_1\rangle - |r_2\rangle - |r_3\rangle) \\ \psi_4 = \frac{1}{\sqrt{2}}(|r_2\rangle - |r_3\rangle) \end{cases} & \quad (11)
 \end{aligned}$$

Regrouping the terms of matrix (10) in terms of the functions (11) we obtain the matrix (12).

$$\begin{array}{c|cccc}
 & \langle \psi_1 | & \langle \psi_2 | & \langle \psi_3 | & \langle \psi_4 | \\
 \begin{array}{l} | \psi_1 \rangle \\ | \psi_2 \rangle \\ | \psi_3 \rangle \\ | \psi_4 \rangle \end{array} & \nu_D & \sqrt{3\nu'_{H-D}} & 0 & 0 \\
 & \sqrt{3\nu'_{H-D}} & \nu_H + 2\nu'_{H-H} & 0 & 0 \\
 & 0 & 0 & \nu_H - \nu'_{H-H} & 0 \\
 & 0 & 0 & 0 & \nu_H - \nu'_{H-H}
 \end{array} \quad (12)$$

Applying standard perturbation arguments,* we may immediately write the

eigenvalues of (12) as $\nu_D - \frac{3(\nu'_{H-D})^2}{\nu_H - \nu_D} (A_1)$, $\nu_H + 2\nu'_{H-H} + \frac{3(\nu'_{H-D})^2}{\nu_H - \nu_D} (A_1)$, and

*The 'repulsion' of interacting energy levels and the particular form of the zeroth- and first-order perturbation energies may be neatly illustrated by a calculation similar to many of those in this article. Suppose that we have to solve the general two-eigenvalue problem summarized in the determinant

$$\begin{vmatrix} A - E & C \\ C & B - E \end{vmatrix} = 0$$

A quadratic equation is obtained on expansion of the determinant:

$$\begin{aligned}
 (A - E)(B - E) - C^2 &= 0 \\
 E^2 - (A + B)E + (AB - C^2) &= 0
 \end{aligned}$$

Then:

$$\begin{aligned}
 2E &= (A + B) \pm \sqrt{[(A + B)^2 - 4(AB - C^2)]} \\
 &= (A + B) \pm \sqrt{[(A + B)^2 + 4C^2]}
 \end{aligned}$$

Now if $A = B$, then $E = A \pm C$

but if $A \gg B$, then we may write:

$$\begin{aligned}
 2E &= (A + B) \pm (A - B) \sqrt{\left[1 + \frac{4C^2}{(A - B)^2}\right]} \\
 &= (A + B) \pm (A - B) \left[1 + \frac{2C^2}{(A - B)^2} + \dots\right] \\
 &\approx (A + B) \pm \left[A - B + \frac{2C^2}{(A - B)}\right]
 \end{aligned}$$

Whence

$$E \approx A + \frac{C^2}{(A - B)} \text{ or } B - \frac{C^2}{(A - B)}$$

Note that, since $A > B$, the perturbations automatically cause a repulsion of levels. Intermediate cases, where $A - B \approx C$, must be solved exactly to give eigenvalues between the above limits.

$\nu_H - \nu'_{H-H}(E)$ if $\nu_H - \nu_D \gg \nu'_{H-D}$. The expression for the eigenvalues of the type- E functions are identical to those for the T_2 functions of CH_4 , but the A_1 functions are different. The reduction in symmetry leads to more mixing with other motions than in CH_4 but this is again neglected. Furthermore the eigenvalues of (12) incorporate four different parameters and only three frequencies are available experimentally. It is precisely because the topology of the interactions of CH_4 and CH_3D vibrations are almost identical, and therefore $\nu'_{H-H} \approx \nu'_{H-D}$, that we can attempt to solve the problem in the same way as the corresponding CH_4 problem. The reader will appreciate immediately the greater difficulties in treating the isomorphous problem of CH_3Cl for which two topological parameters are needed.

The relevant frequencies observed for CH_3D are 2982 (A_1), 3030 (E), and 2205 cm^{-1} (A_1),¹² which may be compared with the corresponding modes of CH_4 , namely the A_1 mode at 2914 cm^{-1} and the T_2 mode at 3020 cm^{-1} . If we equate the three observed frequencies to $\nu_H + 2\nu'_{H-H}$, $\nu_H - \nu'_{H-H}$, and ν_D , respectively, we obtain values of 3016, 2205, and -16 cm^{-1} for ν_H , ν_D , and ν'_{H-H} . The corresponding values of ν_H and ν'_{H-H} of CH_4 are 2994 and -26 cm^{-1} . If we assume that $\nu'_{H-D} \approx -16 \text{ cm}^{-1}$ also, then the term $3(\nu'_{H-D})^2/\nu_H - \nu_D$, which we have neglected, may be seen to have a value only of the order of 1 cm^{-1} . The value of ν'_{H-H} for CH_3D obtained in this way appears to be strikingly different from the value obtained for CH_4 . The difference in the *effective* ν'_{H-H} values reflect the limitations of some of our approximations in which deformation modes are neglected. In particular, there is an important interaction in CH_4 and CH_3X compounds between the A_1 C—H stretching fundamental and the overtone of one of the asymmetric C—H deformations. In CH_3D the latter is found at 1477 cm^{-1} ($2 \times 1477 = 2954$) and therefore perturbs the A_1 fundamental to higher energy, whereas in the corresponding case of CH_4 ($2 \times 1526 = 3052$) the A_1 fundamental is only slightly perturbed to lower energy by this interaction. The values of ν_H for CH_2D_2 and CHD_3 are 2997 and 2992 cm^{-1} , respectively,¹² (*cf.* 2994 and 3016 cm^{-1} for CH_4 and CH_3D).

The approximations which are required increase rapidly with molecular complexity and with any reduction of symmetry. Under these conditions, the number of independent energy parameters required to describe the system rapidly exceeds the number of independent experimental data, and the information obtained from symmetric and topological arguments is correspondingly diminished.

B. Planar Systems. (i) *Hückel Energies of Cyclobutadiene.* The D_{4h} character table appropriate to this and later problems is given in Table 3.

We associate with each point in the system the Coulomb integral, α . In the topological matrix it is necessary to distinguish between the pairs of points which are *cis* and *trans* to one another. We therefore require two resonance integrals β_c and β_t to distinguish the two cases. The basis set $\phi_1 - \phi_4$ is taken to consist of the four out-of-plane (local p_y , molecular p_z) orbitals of the carbon atoms which are numbered sequentially around the square. The remaining

Table 3 D_{4h} Character table

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Rotations	Vectors	Vector products
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	$x^2 - y^2$	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		xy	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	(R_x, R_y)	(xz, yz)	
E_g	2	0	-2	0	0	2	0	-2	0	0			
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		z	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1			
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	-1			
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1			
E_u	2	0	-2	0	0	-2	0	2	0	0		(x, y)	

orbitals all lie in the plane of the molecule and are regarded as 'framework' and/or non-bonding orbitals. The energy matrix is given in (13).

$$\begin{array}{l}
 \langle \phi_1 | \\
 | \phi_1 \rangle \\
 | \phi_2 \rangle \\
 | \phi_3 \rangle \\
 | \phi_4 \rangle
 \end{array}
 \begin{array}{cccc}
 \langle \phi_1 | & \langle \phi_2 | & \langle \phi_3 | & \langle \phi_4 | \\
 \alpha & \beta_c & \beta_t & \beta_c \\
 \beta_c & \alpha & \beta_c & \beta_t \\
 \beta_t & \beta_c & \alpha & \beta_c \\
 \beta_c & \beta_t & \beta_c & \alpha
 \end{array}
 \quad (13)$$

The set of four p_y orbitals transform as $A_{2u} + B_{2u} + E_g$. The orthonormal combinations of ϕ_1 — ϕ_4 are given by (14). The reader should note that this set is also isomorphic to (1).

$$\begin{array}{l}
 A_{2u} + \psi_1 = \frac{1}{2} (\phi_1 + \phi_2 + \phi_3 + \phi_4) \\
 B_{2u} \quad \psi_2 = \frac{1}{2} (\phi_1 - \phi_2 + \phi_3 - \phi_4) \\
 E_g \quad \left\{ \begin{array}{l} \psi_3 = \frac{1}{2} (\phi_1 + \phi_2 - \phi_3 - \phi_4) \\ \psi_4 = \frac{1}{2} (\phi_1 - \phi_2 - \phi_3 + \phi_4) \end{array} \right.
 \end{array}
 \quad (14)$$

With these functions we immediately obtain the eigenvalues of this general topological problem as $\alpha + 2\beta_c + \beta_t$ (A_{2u}), $\alpha - 2\beta_c + \beta_t$ (B_{2u}) and $\alpha - \beta_t$ (twice, E_g). In Hückel theory it is conventional to set the resonance integrals between non-adjacent atoms equal to zero and, therefore, for the case of cyclobutadiene, the four π -electrons are allocated to orbitals of the lowest energy to give the configuration $(a_{2u})^2(e_g)^2$. This configuration does not confer great stability as in the corresponding case of the hexagonal system. The spectroscopic transitions $A_{2u} \leftrightarrow E_g$ (E_u) and $E_g \leftrightarrow B_{2u}$ (E_u) are both electric-dipole allowed in (x,y) polarization, whereas the $A_{2u} \leftrightarrow B_{2u}$ transition (B_{1g}) is forbidden. Neither of the allowed transitions would involve a change in electron-repulsion energy so that it is hypothetically possible to determine the quantity β_c exactly for this unknown molecule.

(ii) *Stretching Vibrations of XeF₄*. This problem is isomorphic to the previous one, but the interaction constant ν'_t can no longer be neglected. Indeed, as the *trans*-ligand atoms in such molecules tend to form bonds involving the same orbitals of the central atom, it is very probable that $|\nu'_t| > |\nu'_c|$. The four stretching modes ψ_1 — ψ_4 which are isomorphic to the set (14) transform as A_{1g} , B_{1g} , and E_u , respectively. From the observed¹⁷ Raman and i.r. frequencies of XeF₄ [543 (R, p), 502 (R, dp), 586 cm⁻¹ (i.r.)] we calculate the values of the three parameters as $\nu = 554$, $\nu'_c = 10$, and $\nu'_t = -32$ cm⁻¹.

(iii) *Other Polygons*. In Table 4 we give general solutions of topological matrices for polygons up to the hexagon, distinguishing between the central, peripheral, and the out-of-plane interactions. The local z -axes point directly to the centre

¹⁷ K. Nakamoto, 'Infra-red Spectra of Inorganic and Co-ordination Compounds,' 2nd Edn., Wiley, London, 1970.

Table 4 General expressions for the eigenvalues of topological matrices for regular polygons

System	Central interactions (sp_z)		Peripheral interactions (p_x)	
	Γ	Eigenvalue	Γ	Eigenvalue
Linear dimer, $D_{\infty h}$	Σ_g^+	$\alpha + \beta$		
	Σ_u^+	$\alpha - \beta$		
Equilateral triangle, D_{3h}	A_1'	$\alpha + 2\beta$	A_2'	$\alpha' - 2\beta'$
	$E'^* a$	$\alpha - \beta$	E'^*	$\alpha' + \beta'$
Square, D_{4h}	A_{1g}	$\alpha + 2\beta_c + \beta_t^b$	A_{2g}	$\alpha' - 2\beta_c' - \beta_t'$
	B_{1g}	$\alpha - 2\beta_c + \beta_t$	B_{2g}	$\alpha' + 2\beta_c' - \beta_t'$
	E_u^*	$\alpha - \beta_t$	E_u^*	$\alpha' + \beta_t'$
Pentagon, D_{5h}	A_1'	$\alpha + 2\beta_o + 2\beta_m$	A_2'	$\alpha' - 2\beta_o' - 2\beta_m'$
	$[g = \frac{1}{2}(\sqrt{5} + 1), E_1'^*]$	$\alpha + g'\beta_o - g\beta_m$	$E_1'^*$	$\alpha' - g'\beta_o' + g\beta_m'$
	$[g' = \frac{1}{2}(\sqrt{5} - 1) E_2'^*]$	$\alpha - g\beta_o + g'\beta_m$	$E_2'^*$	$\alpha' + g\beta_o' - g'\beta_m'$
Hexagon, D_{6h}	A_{1g}	$\alpha + 2\beta_o + 2\beta_m + \beta_p$	A_{2g}	$\alpha' - 2\beta_o' - 2\beta_m' - \beta_p'$
	E_{2g}^*	$\alpha - \beta_o - \beta_m + \beta_p$	E_{2g}^*	$\alpha + \beta_o' + \beta_m' - \beta_p'$
	B_{1u}	$\alpha - 2\beta_o + 2\beta_m - \beta_p$	B_{2u}	$\alpha' + 2\beta_o' - 2\beta_m' + \beta_p'$
	E_{1u}^*	$\alpha + \beta_o - \beta_m - \beta_p$	E_{1u}^*	$\alpha' - \beta_o' + \beta_m' + \beta_p'$

^a An asterisk indicates the existence of an additional cross-term (usually small).

^b $c = cis$; $t = trans$; $o = ortho$; $m = meta$; $p = para$.

of the polygon. Note the similarity of the algebraic expressions of related eigenvalues for each set of interactions; the absolute values of the α^i and the β^j will, however, differ for each case.

C. Molecular Orbitals of an Octahedral Transition-metal Complex.—We take as our final example the energy levels of an octahedral transition-metal complex. It is well known that for this system the crystal-field theory predicts a splitting of the ten-fold degenerate 2D state (*i.e.* d^1 or d^9 configurations) into 2E_g and $^2T_{2g}$ states separated by the frequently parameterized quantity $10Dq$. The molecular orbital approach is even more valuable since it provides scope for consideration of both σ - and π -bonding effects on these two states and also information on a number of important excited states.¹⁰ The pictorial description of the crystal field, which invokes orbital destabilization through repulsive interactions with ligand electrons, is clearly topological in essence and the same is true of the qualitative molecular orbital description. It is also interesting that Schmidtke, perhaps recognizing that the σ - and π -bonding interactions are topologically equivalent to strong ligand–ligand repulsion interactions along the edges of the octahedron combined with metal–ligand σ -bonding as a perturbation, has shown that a similar sequence of energy levels may be obtained by either method.¹⁸

4 Concluding Remarks

Before we tackle any problem of high symmetry it is always advantageous and

¹⁸ H. H. Schmidtke, *J. Chem. Phys.*, 1968, **48**, 970.

Out-of-plane interactions (p_y)

Γ	Eigenvalue
Π_g	$\alpha'' - \beta''$
Π_u	$\alpha'' + \beta''$
A_2''	$\alpha'' + 2\beta''$
E''	$\alpha'' - \beta''$
A_{2u}	$\alpha'' + 2\beta_c'' + \beta_t''$
B_{2u}	$\alpha'' - 2\beta_c'' + \beta_t''$
E_g	$\alpha'' - \beta_t''$
A_2''	$\alpha'' + 2\beta_o'' + 2\beta_m''$
E_2''	$\alpha'' + g'\beta_o'' - g\beta_m''$
E_2''	$\alpha'' - g\beta_o'' + g'\beta_m''$
B_{2g}	$\alpha'' - 2\beta_o'' + 2\beta_m'' - \beta_p''$
E_{1g}	$\alpha'' + \beta_o'' - \beta_m'' - \beta_p''$
A_{2u}	$\alpha'' + 2\beta_o'' + 2\beta_m'' + \beta_p''$
E_{2u}	$\alpha'' - \beta_o'' - \beta_m'' + \beta_p''$

Transformation properties of orbitals at centroid

s	p	d
Σ_g^+	$\Sigma_u^+ + \Pi_u$	$\Sigma_g^+ + \pi_g + \Delta_g$
A_1'	$E' + A_2''$	$A_1' + E' + E''$
A_{1g}	$A_{2u} + E_u$	$A_{1g} + B_{1g} + B_{2g} + E_g$
A_1'	$E_1' + A_2''$	$A_1' + E_2' + E_1''$
A_{1g}	$A_{2u} + E_{1u}$	$A_{1g} + E_{1g} + E_{2g}$

sometimes necessary to decide the basis set for the problem on energetic grounds and to select the topology of the important interactions within this basis set. The topological matrix is then divided into two parts which depend respectively on the symmetry of the problem and the magnitude of the energy terms. The first part of the problem may be solved exactly, but the second part becomes increasingly empirical as the complexity of the problem increases and/or the symmetry decreases. In some cases the interactions between equivalent members of the basis set are not the most important, but in many others a system may be accurately described by the solutions of a simple topological matrix. Such a case is the familiar π -bonding problem of aromatic hydrocarbons. At the other extreme we note the low significance of many ligand-ligand interactions and of the vibronic coupling in many cases where a static distortion is predicted by the Jahn-Teller theorem.

We have given examples of the profound influence of relative energy on the whole basis of a problem and its manner of solution. We may comment additionally that topological considerations are more readily introduced into some problems, such as spin-coupling, than into others such as the π -interactions of the tetrahedron. Topological considerations enter neatly into a valence-bond model, whereas the application of symmetry in this case is seriously complicated by frequent non-orthogonality of the basis set of orbitals. Conversely, in a molecular orbital discussion the symmetry is readily introduced but often this is at the cost of a non-intuitive topology in addition to the problems associated with the neglect of configuration interaction in polyelectronic systems. Neither the symmetry nor the topology of a problem is usually introduced explicitly into a self-consistent-field calculation, as the former is not readily used to shorten the process time and the latter is not required as a conceptual aid! Conversely,

the general *discussion* of any problem is facilitated by distinguishing those parts of the problem which involve the symmetry, the topology, and the energy terms appropriate to the problem in a fully complementary manner. The general solutions of common topological matrices in high-symmetry systems may be used in this way to treat many diverse problems, once the energetic considerations have been clarified.